STUDY ON THE EFFECT OF ZEOLITE RICE HUSK PARTICLES ON POLYSULFONE MEMBRANE

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ABSTRACT

Rice Husk Zeolite Type Y (RHY) particles were prepared under static hydrothermal conditions by dissolution of sodium hydroxide (NaOH), sodium aluminate ($NaAlO_2$) and amorphous silica obtained from rice husk ash (RHA). The RHY/polysulfones (PSf) membranes incorporated with RHY particle at different loading were prepared through phase inversion technique. Physical characterization were carried out using thermogravimetric analysis (TGA), scanning electron microscope (SEM), porosity, tensile strength, atomic force microscope (AFM) and water contact angle (CA). The X-ray diffraction (XRD) analysis confirmed the transformation of RHA into zeolite type Y supported with Field Emission Scanning electron microscopy (FESEM) image and Energy dispersive X-ray spectroscopy (EDX). The EDX analysis showed that the Si/Al ratio was 2.007 which indicate the zeolite products is in hydrophilic condition. Meanwhile, the performance of the fabricated membrane was evaluated through pure water permeation (PWP), rejection and antifouling properties. The membranes with 2wt% of RHY showed the highest water permeability (315.29 $Lm^{-2}h^{-1}$), hydrophilicity (45^{o}) porosity (41.5%) and good rejection (97.8%) ability. Membranes with higher RHY content (more than 2wt. %) generated more particle agglomeration that disturbs membrane structure as can be observed in the cross-section and external surface morphology. In fact, the excessive amount of RHY particles caused deduction of membrane permeation, compared to the pristine membrane which indicated the ability of membrane to absorb the foulants. The incorporation of RHY (1 to 5wt. %) increase the humic acid rejection from 95.8 to 99.6 %. It also found that PSf-RHY membrane having higher absorptive and fouling values than pristine PSf membrane. It can be concluded that the addition of RHY could enhance the hydrophilicity of the PSf membrane with optimum value of 2 wt.%. However, the addition of RHY need to be properly controlled as the high RHY loading could create an adverse effect for the foulants.

ABSTRAK

Zeolite sekam padi jenis Y telah disediakan di bawah keadaan statik hidroterma dengan pelarutan NaOH, $NaAlO_2$ dan silika amorfus dari abu sekam padi (RHA). RHY/polisulfon (PSf) membrane telah dicampurkan dengan zarah RHY pada muatan yang berbeza, disediakan menerusi kaedah fasa penyongsangan, Ciri-ciri fisikal membran dianalisis dengan Termogravimetri (TGA), mikroskop imbasan elektron (SEM) , jelmaan fourier infra-merah (FTIR), keliangan, ujian kekuatan tegangan, mikroskop kuasa atom (AFM) dan pemerhatian sudut sentuhan air (CA). Analysis XRD mengesahkan transformasi RHA kepada zeolit Y disokong dengan hasil imej FESEM dan EDX. EDX menunjukkan nisbah Si/Al adalah 2.007 menyatakan bahawa produk zeolite adalah bersifat hidrofilik. Sementara itu, ujian prestasi yang telah dijalankan dengan kaedah ketelapan air suling (PWP), ujian penolakan dan ciri-ciri anti-kotor. Pada kandungan 2wt% RHY, membran mengalami kebolehtelapan air yang tertinggi (315.29 $Lm^{-2}h^{-1}$), hidrofilik (47.5^{o}) keliangan (41.5%) dan penolakan yang baik (97.8%). Kandungan RHY yang tinggi (melebihi 2wt%) menyebabkan penggumpalan zarah pada struktur membran berdasarkan pemerhatian keratan rentas dan morfologi permukaan luar membran yang terhasil. Malah, kandungan lebihan RHY menyebabkan penurunan ketelapan membran berbanding membran asli dan ini menunjukkan kebolehupaya membrane tersebut menyerap kotoran.. Penambahan RHY (1 hingga 5wt.%) meningkatkan penolakan asid humik dari 95.8 kepada 99.6%. Ia juga menunjukkan bahawa PSf-RHY membran mempunyai penyerapan dan nilai kotoran yang lebih tinggi berbanding membran PSf yang asli. Ia boleh disimpulkan bahawa penambahan RHY boleh meningkatkan ciri hidrofilik kepada PSf membran pada nilai optimum iaitu 2%. Bagaimanapun, penambahan RHY perlu dikawal dengan betul kerana lebih tinggi kehadiran RHY ini menyebabkan kesan sebaliknya terhadap serapan kotoran.

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LIST OF ABBREVIATIONS

PSf	-	Polysulfone
PVDF	-	Polyvinylidene fluoride
RH	-	Rice husk
RHA	-	Rice husk ash
RHY	-	Rice Husk Zeolite Type Y
RHS	-	Rice husk silica
TIPS	-	Thermally Induced Phase Separation
MMMs	-	Mixed Matric Membranes
NaOH	-	Sodium hydroxide
$NaAl_2O_3$	-	Sodium aluminate
H_2SO_4	-	Acid sulfuric
HCL	-	Hydrocloric acid
pH	-	$-\log[H^+]$
rpm	-	Revolution per minute
MW	-	Molecular weight
RHY		Synthesized Rice Husk Zeolite Type Y
NMP	-	N-methyl-2-pyrrolidone
UF	-	Ultrafiltration
PEG	-	Polyethylene glycol
FTIR	-	Fourier transform-infrared
TGA	-	Thermalgravimetric test
FESEM	-	Fied Emission Scanning electron microscopy
SEM	-	Scanning electron microscopy
AFM	-	Atomic Force
UV	-	Ultra-violet
NF	-	Nanofiltration
RO	-	Reverse osmosis
MF	-	Microfiltration

PEG	-	Polyethylene glycol
XRF	-	X-ray Fluorescence
XRD	-	X-ray diffraction
AFM	-	Atomic Force Microscopy
EDX	-	Energy dispersive X-ray spectroscopy
Q	-	Permeate volume (L)
A	-	Membrane Area (m^2)
Δt	-	Time (h)
Wt%	-	Weight Percentage
PWP	-	Pure Water Permeation
J_O	-	Pure Water Flux of clean Membrane
J_f	-	Pure Water Flux of Fouled Membrane
HA	-	Humic Acid
CP	-	Concentration polarization
TiO_2	-	Titanium dioxide
SiO_2	-	Silica Oxide
ZnO	-	Zinc oxide
Si	-	Silicon
Al	-	Aluminium
ICDD	-	International Centre for Diffraction Data
JCPDS	-	Joint Committee on Powder Diffraction Standards
CA	-	Contact Angle
Eq.	-	Equation
GO	-	Graphite Oxcide
PV	-	Pervaporation
Na	-	Sodium
Li	-	Lithium
K	-	Kalium
Rb		Rubidium
Cs		Caesium

LIST OF SYMBOLS

%	-	percent
^{O}C	-	degree celcius
hr	-	hour
^{o}	-	degree
θ	-	theta
wt. %	-	weight percentage
r_m	-	mean pore diameter
ε	-	porosity
μm	-	micrometer
nm	-	nanometer
ml	-	milimeter
g	-	gram
Q	-	volume permeate
A	-	Membrane surface area
ΔT	-	Permeation time
C_p	-	Concentration of permeate
C_f	-	Concentration of feed
J_{wf}	-	Pure water flux permeation
Pas	-	Pascal second
Rm	-	Membrane resistance
Rc	-	Cake resistance
Rcp	-	CP resistance
Ra	-	Absorption resistance
Rt	-	Total resistance
C	-	Carbon
S	-	Sulfur
Al	-	Aluminum
Si	-	Silicon

ρ_w	-	Water density
V	-	Volume
w_w	-	Weight during wet
w_d	-	Weight during dry

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CHAPTER 1

INTRODUCTION

1.1 Introduction of Membrane

One of the main challenges of the 21st century, especially in developing countries, is lack of access to clean water. Improved separation technologies can be expected to reduce the amount of waste emissions, particularly in the area of separation from dilute streams. Industrial wastes may contain oil, organics and grease as common pollutants that generated from wide range of industries. Separation technology via membrane technique offers a better way in treating the polluted industrial stream that may contain organic mixtures i.e. bacteria. Membrane technology is widely used and known at the middle of the eighteenth century where it was critically observed and studied by many researchers.

However, the adsorption and deposition of foulants in membrane surface and pore walls, often serve the decreament of flux. This membrane technology is seriously limited by membrane fouling. In recent years, many researcher have revealed that increasing the hydrophilicity of the membrane surfaces and pore surfaces remarkably reduce or supress membrane fouling (Li *et al.*, 2006; Rana & Matsuura, 2010; Razmjou *et al.*, 2011). Several methods, including the adsorption, coating, grafting polymerization and blending are comprising the established routes for membrane modification (Leo *et al.*, 2012). For example, blending allows membrane modification during the fabrication phase. Blending is also considered to be the simplest method among the other methods, involving physical mixing of polymer with hydrophilic element. The hydrophilic element is meant to be a hydroplic polymer or inorganic oxide. By blending this two element changes the membrane properties not only for hydrophilic properties, also permeability, selectivity, mechanical strengh, and thermal resistance (Yong *et al.*, 2013).

Despite the usefulness of hydrophilic element in membrane modification, their application in providing great membrane performance is still an issue to be tackled. Recently, many studies have been conducted to select the most effective and compatible additive as well as to resolve membrane fouling problems. As a result, the selection of hydrophilic element is the most crucial thing to solve fouling problem as well as great in permeability and selectivity.

1.2 Project Background

In membrane technology, it is very important to control membrane structure and property as these criteria strongly affect the overall membrane performance such as flux and rejection. Generally, membrane can be developed via various polymeric materials and methods. Development of polymer materials through several modification offer a good properties and structure definitely benefit to other polymer application especially in membrane preparation. Thus, in this work polymer blending is chosen as main raw material since it has great properties considering of more compatibly in membrane preparation process. In fact, combination of different polymer materials can gives better performance and mechanical properties than that of membrane composed by the original individual polymers (Alsalhy, 2012).

One of the main problem or critical situation aforementioned is fouling mechanism. In general, the membranes fouling will shorten the life of membrane, result in the rising of cost of maintenance, which definitely will obstruct its large-scale applications in the industry. Consequently, searching and developing new membrane materials and method/technique in order to suppress the membrane fouling and increase antifouling are highly needed. Hydrophillicity is one of the desirable properties of membrane which can mitigate membrane fouling. This is due to polymeric materials used for membrane fabrication mostly is weakly hydrophilic (Wang *et al.*, 2011). For example Polysulfone (PSf) is widely used as a microfiltration (MF) and ultrafiltration (UF) membranes in many industrial fields has hydrophobic property but frequently used due to their low cost, superior film forming ability, good mechanical and anti-compaction properties, strong chemical and thermal stabilities, and outstanding acidic or alkaline resistance (Lau *et al.*, 1991). This hydrophobic nature always results in severe membrane fouling and decline in permeability

(Summers *et al.*, 2003). Therefore, comprehensive effort has been put to increase the hydrophilicity of membrane via physical or chemical method (Wang *et al*., 2011). The incorporation of inorganic materials into the organic polymer matrix with blend strategy has attracted great interests due to their completely superior membrane performance (Liang *et al.,* 2012). Thus, most attention are focused on membrane structure modification. The structure property of internal pore not only influence the fouling behavior at outer separation layer but also strongly influence the separation inside the membrane structure.

Basically, incorporation of inorganic material in polymer membrane can be classified as mixed -matrix membranes (MMMs). MMMs are excellent candidates to overcome the upper-bound constraint. Most of the research conducted on MMMs focused on the combination of a solid molecular sieving blend phase, such as zeolite or carbon molecular sieve, bulk polymer matrix (Li *et al.*, 2011). The mainly nano-material used in previous study such as, TiO_2 and Al_2O_3 nanoparticle are relatively expensive for practical applications (Razmjou *et al.*, 2012; Shi, *et al.*, 2012; Thuadaij & Nuntiya, 2012; Yan *et al.*, 2006). Here, the incorporation of zeolite mixed into MMMs was investigated to increase membrane performance in order to give better separation since it has a remarkable property towards hydrophilicity, fine membrane and pore surfaces. Perhaps, by adding small amount of zeolite into the polymer matrix would increase significantly the overall separation efficiently.

1.3 Problem Statement

In membrane operation, fouling is one of the most crucial problems that always associated to the failure of membrane separation process. Basic feature of fouling is due to irreversible foulants absorption and can only be resolved to a certain extent by aggressive chemical cleaning. Variety of methods and techniques has been investigated in order to reduce and avoid fouling mechanism. Modifiying the polymer features through blending approach offer a versatile way to increase antifouling effect with new desirable properties, less complicated than developing new polymerization, the least expensive, suitable in operation and easy-going in condition. For instance, a novel of nano-zinc oxide (ZnO) was blended into the membrane matrix for the modification of internal surfaces of membrane pores (Liang *et al*., 2012). The presence

of ZnO modified polyvinylidene fluoride (PVDF) membrane demonstrated significant antireversible fouling property which is related to the increasing of membrane surface hydrophicity. This shows that inorganic material which is highly hydrophilicity incorporate with PVDF membrane greatly improved the properties of the membrane.

Thus in this study, polysulfone (PSf) membrane was incorporated with modified zeolite Y (RHY). RHY zeolite was used in order to enhance more hydrophilicity of membrane. This hydrophilicity of RHY zeolite definitely can enhance antifouling mechanism which indirectly can increase permeability property.

1.4 Objective

The main objectives of this study are:

i. To extract and characterize Zeolite Y from natural rice husk ash (RHA) via hydrothermal process
ii. To characterize and study the properties of fabricated PSf membrane blending with different weight RHY percentage (wt.%) via pahse inversion technique
iii. To determine the performance and properties of fabricated PSf membrane blending with different weight RHY percentage (wt.%)

1.5 Scope of study

i. Extraction technique for RHY is using hydrothermal process
ii. Characterization of Zeolite Y using X-ray Diffraction (XRD), Energy dispersive spectroscopy (EDS), Particle Analyzer and Field Emission Scanning Electron Microscopy (FESEM)
iii. Fabrication of PSf membrane incorporates with RHY particles at 1, 2, 3, 4, and 5 wt.% are carried out using phase inversion technique
iv. Material that used for membrane fabrication is PSf as main polymer material, N-methyl-2-pyrrolidone (NMP) as solvent, PEG 400 as pore forming agent and RHY particles as inorganic additive
v. Viscosity of the dope formulation was measured via viscometer

vi. Physical properties and characterization of MMMs investigated in terms of chemical bonding, thermal degradation, hydrophilicity, microstructure cross section and morphology, mechanical strengh, pore size, porosity, and surface roughness

i. Membrane performance investigated by permeability water flux, humid acid rejection and fouling test within 120 min at room temperature

CHAPTER 2

LITERATURE REVIEW

2.0 Introduction

Membrane filtration promises an efficient and long-term solution for sufficient supply of quality water to meet human, environment, and industrial needs. In the conventional method, membrane filtration includes physical separation techniques for particle removal, biological and chemical treatments; evaporative technique, and other physical and mechanical methods. Membrane separation replaces these techniques by the use of selectively permeable barriers, with pore size to permit the passage of water molecules to pass through but small enough to preserve a broad range of particulate compounds depend on their nature (Basri *et al*.,2011).

Although membrane systems are able to achieve superior product quality, the reduction in separation efficiency always becomes the obstacles. This reduction is mainly due to the membrane fouling mechanism. Thus, membrane fouling remediation becomes the focus of many efforts. Fouling results from complex phenomenon are correlated to the deposition of the component at the surface and inside the porous membrane. The methods applied to reduce these effects include pre-treatment of the feed solution, cautious selection of membrane material, appropriate setting of operational parameters, and the use of turbulence promoters. However, the selection of membrane material in terms of modifying becomes the primary alternative for minimizing the fouling problem. These modifying inclusive incorporation of additives in polymer membrane or known as mixed matrix membranes (MMMs) is promising simple technique for reducing fouling mechanism. Fouling could be reduced by modifying the membrane features to avoid the adhesion of foulant on the membrane surface directly by blocking the filtered water molecule from passing through the membrane pores (Abdelrasoul *et al*., 2013).

2.1 Introduction to Membrane

Basically, a membrane is a semipermeable barrier in which separation occurs by controlling the rate of movement of various molecules between two liquid phases, two gas phases or a liquid and a gas phase (Geankoplis, 2003). From structural point of view, the morphology of a membrane is broadly divided into two which is symmetric (or isotropic) and asymmetric (or anisotropic) (Gosh, 2006). The thicknesses of symmetric and asymmetric membrane usually (porous or nonporous) range approximately from 10 to 200 μm (Mulder. M., 1991). While the pore sizes may vary from 1nm to 50 μm. The membrane structure is portrayed by the pore size, shape, distribution, charge, and other features (Razmjou *et al*., 2011).

Membranes have been developed for various applications (Ismail & Lai, 2004; Li & Wang, 2010; Zeng et *al.*, 2008), including desalination, gas separation, filtration, dialysis, and others. Every application requires specific requirements on the membrane material and structure. For microfiltration and ultrafiltration membranes, porosity and pore sizes of the membrane are important in determining the efficiency of the process. In terms of materials, membranes could be made from polymers, ceramic, and even metal(Dey *et al.*, 2013; Van Gestel, *et al.*, 2006).

Basically, this study focuses on polymeric porous membrane, which separates the pollutant by its pore size and pore distribution as in Figure 2.1. The polymeric membrane with pore size > 50 nm is normally used for microfiltration and membranes with pore size between 3 nm – 100 nm are used for ultrafiltration while the membranes with pore size around 1 nm are used for nanofiltration. In terms of pore distribution, asymmetric membranes mostly have similar pore sizes. Asymmetric membranes also consist a very dense top layer or skin with small pores supported with porous sublayer with larger pores.

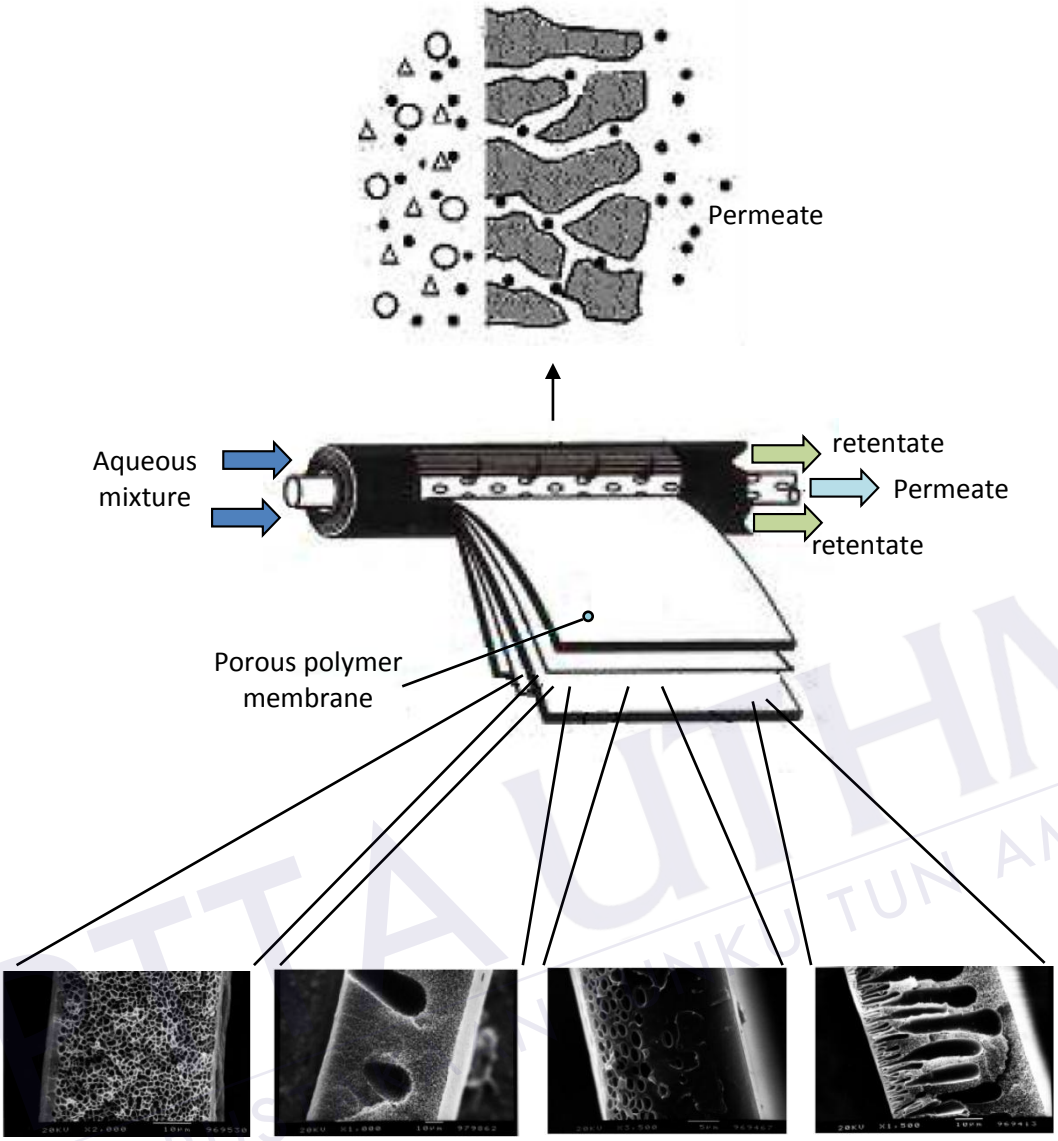

Figure 2.1: Membrane with varied pore sizes and distribution (Huang *et al.*, 2012) (Kools, 1998)

2.2 Membrane Formation

In order to achieve the desired membrane properties, the mode of preparation plays a vital role. Several techniques could be used such as sintering, stretching, track etching, phase inversion, and coating. Depending on the materials and the process conditions, different techniques could give different membrane morphology. In the case of polymeric membrane, the most technique that has been used is phase inversion process.

2.2.1 Phase Inversion Methods

In the phase inversion process, the polymer is transformed in a controlled manner from a liquid to a solid state in a controlled manner. The process of solidification is very often initiated by the transition from one liquid state into two liquids (liquid-liquid demixing). At a certain stage during demixing, one of the liquid phases (the high polymer concentration phase) will solidify so that a solid matrix is formed.

In the process of phase inversion, the polymer solution may be participated by different approaches, including cooling, immersion in a non-solvent coagulation bath, evaporation, and vapour adsorption as well. Before discussing the selected phase separation processes in detail, a short survey of the four main techniques for the preparation of polymeric membranes preparation by controlling the phase separation is presented as follows (Witte et al.et al., 1996) :

1. **Thermally induced phase separation (TIPS)**. This method is based on the phenomenon that the solvent quality usually decreases when the temperature is decreasesd. After demixing is induced, the solvent is removed by extraction, evaporation or freeze drying.
2. **Air-casting of a polymer solution**. In this process, the polymer is dissolved in a mixture of a volatile solvent and a less volatile non-solvent. During the evaporation of the solvent, the solubility of the polymer decreases, and then the phase separation can take place.
3. **Precipitation from the vapour phase**. During this process, phase separation of the polymer solution is induced by the penetration of non-solvent vapour in the solution.
4. **Immersion precipitation**. A polymer solution is casted as a thin film on a support or extruded through a die, and is subsequently immersed in a non-solvent bath. Precipitation can occur because the good solvent in the polymer solution is exchanged for to non-solvent.

The differences of the four techniques originate from the differences in desolvation mechanism. A phase diagram can predict whether if or not the solution of a certain polymer in a certain solvent is suitable for membrane formation.

2.2.2 Immersion Precipitation Process

The immersion precipitation technique is one of the most techniques used in microporous anisotropic membrane preparation. This technique is rather simple and is based on the immersion of a polymer film, cast onto a suitable support in a non-solvent bath as illustrated in Figure 2.2 (Di Luccio et al., 2000).

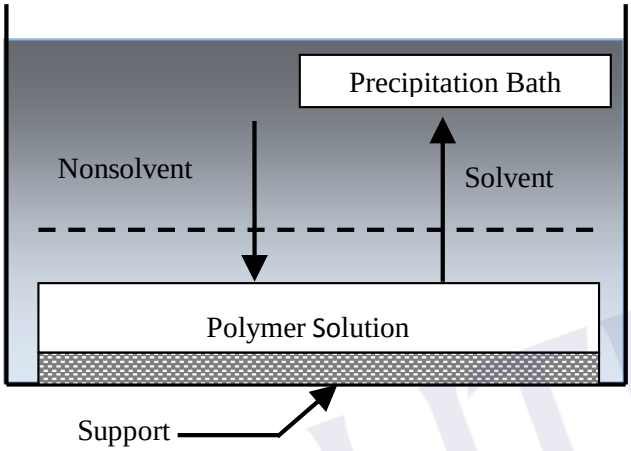

Figure 2.2: Schematic depiction of the immersion precipitation process (Di Luccio *et al.*, 2000)

According to Chakrabarty *et al.*, (2008), immersion precipitation is a homogeneous polymer solution casts on a suitable support as a thin film and then immersed into a coagulation bath containing suitable non-solvent (Figure 2.2). At this stage, a thermodynamically stable polymer solution solidifies to form a membrane with a symmetric or asymmetric structure through the exchange between the solvent inside the cast film and the non-solvent outside the cast film in the coagulation bath. In this process of solidification, the film goes through the complicated phase changes. (The schematic ternary phase diagram and the resulting composition of the polymer solution are shown in Figure 2.3)

The basic thermodynamic of the immersion precipitation method is a phase diagram of non-solvent/solvent/polymer system and it has been well developed (Mulder, 1991). From Figure 2.3, the polymer solution is placed in the stable region outside the binodal. The 'binodal demixing', specifically by pathway A, is the most fundamental phase separation mechanism in which the polymer solution is in the metastable region, in between the binodal and spinodal. At this area, the polymer solution divides into polymer-lean and polymer-rich phase, indicate by the A' and A"

tieline ends, respectively. Polymer-rich phase turns into a solid matrix by crystallization or vitrification, while the polymer-poor phase develops into the pores. Spinodal decomposition, the second and less frequent mechanism is represented by pathway B. This takes place whenever the polymer solution directly moves to the thermodynamically unstable zone within the spinodal. Again, two different phases are formed, but instead of developing well-defined nuclei, two co-continuous phases are formed.

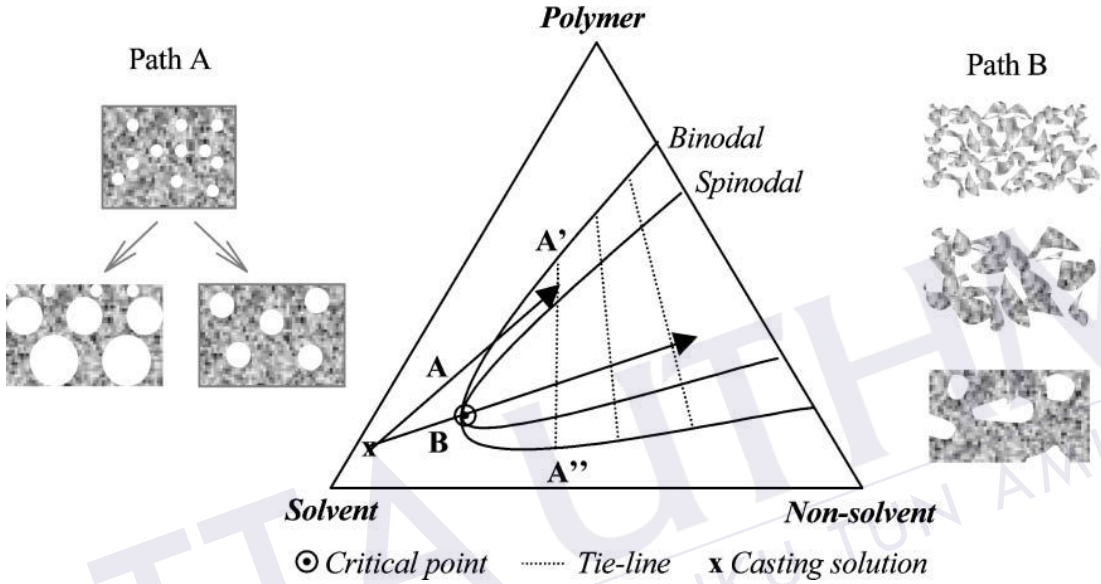

Figure 2.3: Schematic nonsolvent/solvent/polymer ternary phase diagram. The polymer solution starts with 'x' mark (where the solution is still homogenous) and move to tie line due to interdiffussion of nonosolvent and the solvent. Then, the system separates into two phases (A' and A'' on the binodal curve) (Vandezande, *et al.*,2008)

Besides thermodynamic, the kinetic aspects of the phase inversion process should also be considered. More specifically, the moment the membrane structure is converted into a solid state. Figure 2.4 shows the composition path of a cast polymer film (1: top of film; 2: middle; and 3: bottom) in a phase diagram at a specific moment (t), right away after the immersion. As more and more solvent exchange with the non-solvent, a different decomposition path is presented for each following moment. In Figure 2.4 (a), the composition path crosses the binodal at time t, and demixing starts instantly (instantaneous demixing). At this condition, a fine porous membrane structure will develop. In Figure 2.4 (b), however, at time t, all positions in the film

are still in thermodynamically stable region. In this case, demixing begins after a while as more and more non-solvent diffuse into the polymer film in such a way that the binodal can be crossed (delayed demixing).

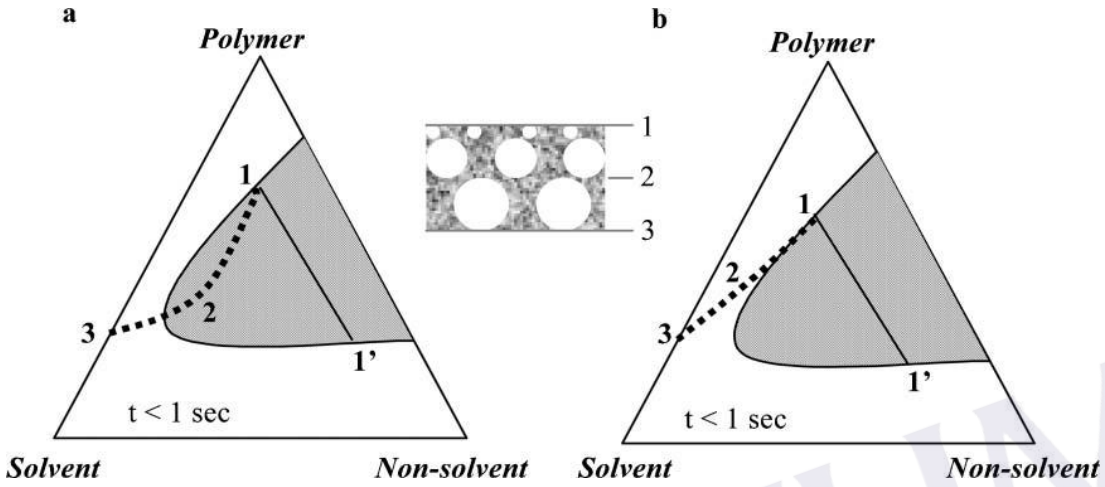

Figure 2.4 : Composition paths of two phase separation processes almost immediately after immersion: (a) instantaneous demixing, (b) delayed demixing (Vandezande *et al.*, 2008)

In terms of structure, membranes that are formed by instantaneous demixing generally have highly porous substructure (with macrovoids) and a finely porous, thin skin layer (Wienk *et al.*, 1996). Nevertheless, they are usually considered as undesired mechanically weak spots in the membrane. The conditions in delayed demixing still show a porous substructure (often closed-cell, macrovoid-free), with a dense and relatively thick skin layer (Chakrabarty *et al.*, 2008). This delayed demixing occurs by selecting a non-solvent with limited miscibility and a solvent in the casting solution, by increasing the polymer concentration in the casting solution or by introducing evaporation step before the immersion of the cast film into coagulation bath.

A variety of experimental parameters have shown to have an impact on final morphology of the membrane, consequently reflected on their performance (Emadzadeh *et al.*, 2014; Liu *et al.*, 2000; Zhao *et al.*, 2014). Casting solution composition is also manipulated by the addition of suitable additives which can be one of the convenient and efficient methods that could be applied based on the previous studies.

2.3 Membrane performance

Membrane performance can be measured in two ways; permeation and rejection mechanism. Both measurements normally show an oppose pattern whereby if the permeation is low, the rejection will be high. This could be related to the blockage or fouling mechanism on the surface or internal membrane structure as the permeation increases. Permeation and fouling are closely interlinked where the effect of uncertainty permeability causes fouling phenomenon. The basic fouling mechanism can be explained by the permeation process.

Permeation mechanism can be defined as a mass transport process where molecules are transferred through the polymer from 'exterior' environment to 'interior' environment, or vice versa, through diffusive process. Mass transport of molecules in a solution or molecular transport across a barrier is usually measured by flux. The flux of a solute is simply defined as the mass or number of molecules moving through a given cross-sectional area during a given period of time.

However, as permeation continue, fouling could arise due to many factors. This fouling may reduce permeate flux, increases feed pressure, and ultimately shortens the membrane life (Schäfer *et al.*, 2004). This phenomenon increases the cost by increasing energy consumption, system-down time, and labour time, as well as increases the material cost for backwashing and cleaning process (Abdelrasoul *et al.*, 2013). Thus, a successful membrane requires an efficient approach to control the fouling problem.

2.4 Fouling mechanism

Fouling is an undesirable phenomenon which is usually caused by adsorption and deposition of material on the membrane. Basically, fouling can be defined as a reduction in water transport per unit area of membrane caused by the accumulation of substances including microorganisms, inorganic, particulates, colloidal, and organic matter on or in the membrane (Lee et al., 2010). In past decade, numerous studies have been performed to investigate and solve these fouling mechanism. The factors contribute to fouling are strongly correlated. Roughly, fouling can be categorized into four types of foulants: (i) organic precipitates (macromolecules, biological substances,

etc.); (ii) colloids; (iii) inorganic precipitates (metal hydroxides, calcium salts, etc.); and (iv) particulates (Field, 2010).

The influence of all of these foulants is made by the consequences of resistance filtration of the membrane. As the fouling resistance increases, it reduces the permeate flux. Numerous techniques have been developed to measure the resistance filtration caused by membrane fouling. Resistance involves for flux decreasing includes membrane resistance (Rm), CP resistance (Rcp), cake resistance (Rc), and pore blocking resistance (Rp). Thus, the total resistance (Rt) during membrane filtration can be stated as:

$$Rt = Rm + Rcp + Rc + Rp \quad (2.1)$$

The types of membrane (i.e. porous versus non-porous) play an important role in determining the resistance for flux decline caused by inorganic fouling. For instance, all four types of resistance (Rm, Rcp, Rc, and Rp,) could be responsible for flux decline of porous membranes. Figure 2.5 shows a schematic diagram of main resistance of a porous membrane during membrane filtration.

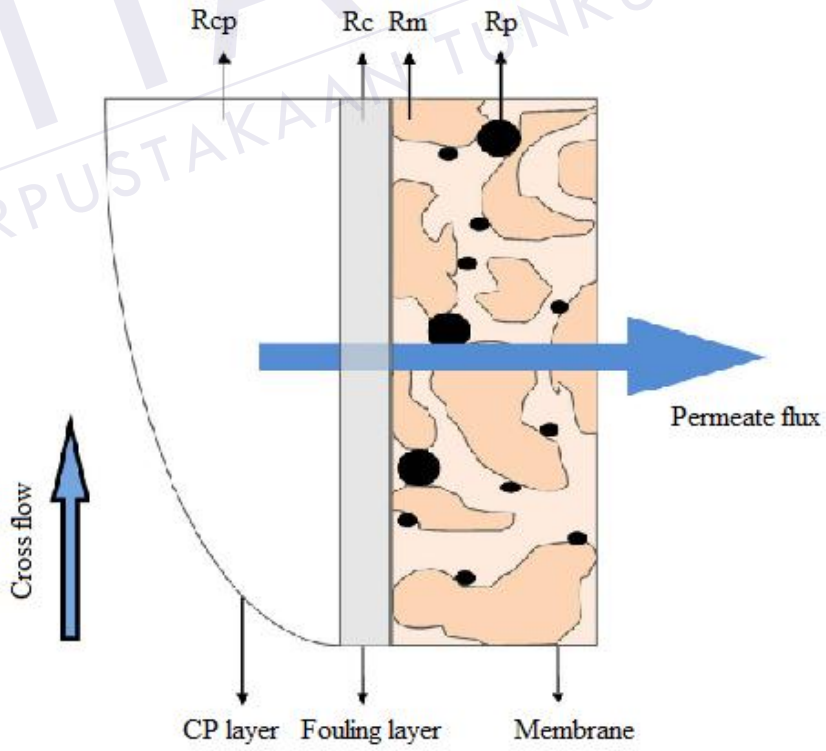

Figure 2.5: Overview of the major resistances of a porous membrane during filtration (Shirazi *et al.*,2010)

Membrane resistance (Rm) is actually caused by the membrane's characteristics. Membrane resistance generally occurs in both, porous and non-porous membranes. The scope of resistance depends on the membrane thickness and the various morphological characteristics such as the tortuosity, porosity, and pore size distribution.

For concentration polarization (Rcp), it is built by the highly concentrated layer near the membrane surface, forces resistance towards the mass transfer, i.e. concentration polarization resistance (CP). Due to the CP, the accumulated solute and particle concentrations turn into a high layer, or called as cake layer. Cake layer can be produced close to the membrane surface, exert the cake resistance. Resistance that is forced by CP triggers to foul on the membrane surface. It is important to distinguish between CP and fouling resistance, although both are not completely independent of each other(Berg & Smolders, 1990; Wijmans *et al.*, 1984).

Meanwhile, cake resistance (Rc) occurs during membrane fouling wherein the foulants (the substance which cause fouling) develop a cake layer at the membrane surface. Rc yield resistance to permeate transportation, leads to permeate flux decline. Pore blocking resistance (Rp) or absorption resistance (Ra) can be can be referred as the foulant that may completely or partially block the membrane pores by the adsorption into the inner wall of membrane pore (Shirazi *et al.*,2010).

In order to reduce and avoid fouling mechanism, various methods and techniques have been investigated. Incorporation of inorganic materials into organic polymer matrix has received the most attention due to its effectiveness and simple technique compared to others. This incorporation or mixed matrix membranes (MMMs) are promising systems for fouling solution due to their significant properties and are produced from the cooperative interaction between the characteristics of the components. The combination of inorganic materials with highly potential organic polymers has attracted a lot of attention over the past few years (Lind *et al.*, 2009; Sorribas, *et al.*, 2013). The MMMs building in polymeric membranes have greatly received interest due to the significant changes in membrane properties such as mechanical (Tsai *et al.*, 2001), thermal (Shi *et al.*, 2013), morphology (Aroon *et al.*, 2010; Basri *et al.*, 2011; Yang *et al*, 2007), hydrophilicity (Nair *et al.*, 2013; Zhao *et al.*, 2011) and antifouling (Basri *et al.*, 2012; Huang *et al.*, 2012; Jamshidi *et al.*, 2014; Shi *et al.*, 2013; Su *et al.*, 2008; Zinadini *et al.*, 2014).

In fact, these inorganic additives can also act as an additive to create a spongy membrane structure by prevention, macrovoid formation, enhance pore formation, improve pore interconnectivity, and introduced hydrophilic element (Tasselli *et al.*, 2005). The mixture with such additives can affect the final membrane and performance of antifouling properties.

2.5 Modification of membrane

Modification of membrane can be done by modifying the dope solution casting in order to gain the desired membrane subject to their application. This modification of dope casting solution involves solvent, polymer concentration, as well as additives.

2.5.1 Solvents

Many polymers can be dissolved in polar aprotic solvents such as 1-methyl -2-pyrrolidone (NMP) N, N-dimethylacetamide (DMAc), N, N-dimethylformamaide (DMF), dimethylsulfoxide (DMSO), etc. (Alsalhy , 2012, Sukitpaneenit & Chung, 2009; Idris *et al.*, 2010; Shen *et al.*, 2005). The choice of solvent is obviously controlled by the polymer type, but the affinity between the solvent in the casting solution and the non-solvent in the coagulation bath is also important for the membrane morphology. Several authors have reported higher flux through asymmetric membranes prepared from NMP-containing casting solutions compared to other containing solutions when using water is used as the immersion medium.

Tweddle *et al.*, 1983 found that among the solvent tested, NMP proved to be a preferable solvent because the polymer-solvent system seems to remain stable for a long time (more than a year). The reason is, after an overnight immersion of the film membrane in water following gelation, subsequent permeation of pure water through the film under pressure for a few hours appeared to remove the remaining solvent from the membrane pores completely, as confirmed by carbon analysis of membrane-permeated water.

Nevertheless, the chances of traces in the solvent remain trapped in the blind pores of the membrane is always there. It has been found that most prepared and

pretreated membranes produce reasonable consistent results. Yet, according to Ahmad *et al.* (2005), NMP is chosen as the solvent due to its strong interaction with polymer and miscibility with water during the addition of other polymeric additives.

2.5.2 Polymer concentration

The concentration of polymer in dope solution also plays an important role due to its relation to shear viscosity during casting process. According to Pesek & Koros (1993), polymer concentration and solvent ratio affect the membrane morphology and separation performance. The increase of polymer concentration at a content solvent ratio produces higher solution viscosity and selectivity, but generally lower pressure-normalized flux. These flux losses were the results of thicker selective skins; and transition layers is believed to be caused by slow redissolution and delayed demixing at the layer of initial phase outermost separated regions of growing membranes from an underlying homogeneous solution (Ahmad *et al.*, 2005).

Understanding the correlations between the final membrane structure and permeation properties and its influence on kinetic viscosity properties of membrane forming system is important to determine polymer concentration. This relation has been explained by Mustaffar *et al.* (2004) wherein the increase of polymer concentration on casting solution leads to an improvement of solution viscosity. The increase of polymer concentration reduces the coagulation value due to the stronger interaction of solvent and polymer; while greater interaction of non-solvent and polymer leads to the decrement of dissolving power of solvent for the polymer. Thus, this would further promote aggregation of polymer molecules through chain entanglement. Both effects would decrease the miscibility of the system as well as enlarge the demixing gap for phase separation, leading to a rapid coagulation rate and an instantaneous phase separation, especially for nascent skin layer that is formed during dry phase separation process.

However, increasing polymer concentration is sometimes advantages to the separation performance of solute particle. Mustaffar *et al.* (2004)) found that the effect of polymer concentration on the flux of hollow fibre ultrafiltration membranes decreases. However, the separation performance of particle solute increases as the polymer concentration increase.

2.5.3 Additives

The addition of third element into casting dope solution which consists of a polymer and a solvent is broadly used as a procedure to develop the flexibility of the phase-inversion process. Co-solvent and additives such as polymers (organic) and inorganic materials have been currently used. This generates extremely complex thermodynamic/kinetic situation which is hard to rationalize and surely expect.

2.5.3.1 Organic additives

The attention regarding the immersion precipitation method for membrane fabrication is mainly focused on the use of organic additives material. Organic additives can suppress or persuade pore formation, depend on their content in the casting dope solution. Non-solvent is one of the organic additives that has been well developed in modifying membrane morphology. By adding non-solvent in small concentration, it induces macrovoid formation, directly increasing the porosity of the membrane. Pesek, & Koros (1994) have enhanced the porosity of PSf membranes by adding two different non-solvents in the polymer dope. The porosity enhancement can be explained by a study done by Smolders *et al.* (1992) where the nucleation of polymer-poor phase was resulted from instantaneous demixing which initiated the formation of macrovoids while delayed demixing made the nuclei grow to form macrovoids.

It can be exemplified by the presence of methanol and n-hexane as a solvent exchange to minimize fibre shrinkage and pore collapse before drying at room temperature (Mansourizadeh & Ismail 2010 It has been reported that the formation of long finger-likes attributed to the fast solidification (instantaneous demixing) resulted from the reduction of the dissolving power of the solvent using additives in the spinning dopes (as in Figure 2.6).

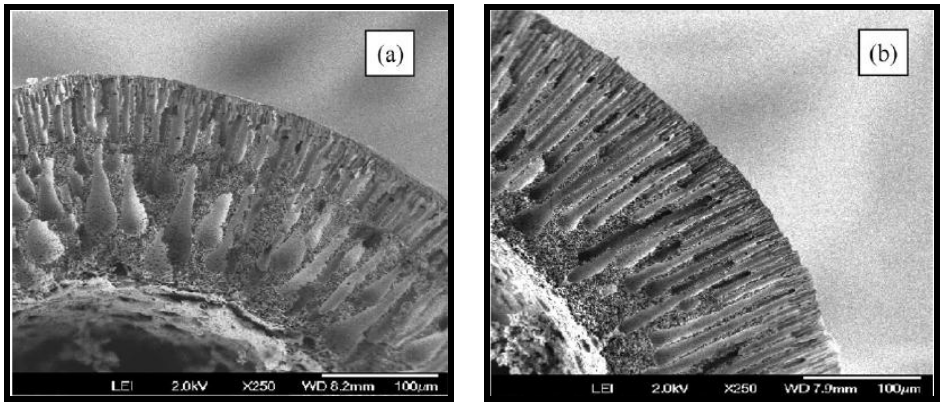

Figure 2.6: FESEM micrograph of cross-sectional structure of the hollow fiber membranes. Different additives in polymer dope (6 wt.%): (a) without additive, (b) ethanol (Mansourizadeh & Ismail, 2010)

Sinha & Purkait, (2014) found that PVDF membranes with the addition of different alcohols (methanol, ethanol, n-propanol, and n-butanol) elevated the pore formation but beyond 5%, less porous membrane were formed. It is important to highlight that the membrane morphology is strongly affected by the amount of non-solvent additives. Reuvers, (1987) reported that sufficient amount of non-solvent additives could improve the formation of macrovoids (finger-like pores) but excessive non-solvent will suppress their formation.

Instead of modifying the non-solvent in membrane formation, the addition of volatile co-solvent in casting solution is one of the techniques offered to enhance the selectivity of a membrane. By letting partial evaporation of the volatile solvent between the casting and immersion step, a skin layer with higher polymer concentration can be formed. Tetrahydrofuron (THF) is one of the examples of volatile solvent used in many studies. It provides the elimination of macrovoid formation during the instantaneous process and selective loss of the THF from the outermost surfaces of freshly cast membrane. The characteristic of THF which is miscible with water and most polymers ease the blending of these materials to form a densified skin-layer (Varghese *et al.,* 2008).

Most of the results data showed that the addition of any type of volatile solvent in casting solution increase the selectivity in gas or water separation causing the skin layer thickness to experience delayed demixing processes. Chen *et al.,* (2007) has reported polarity through the addition of chloroform as a volatile solvent towards PSf membrane resulted in the changes of skin layer thickness. Increasing the amount of

chloroform (a nonpolar solvent) supplied to the PSf/NMP/water ternary system causes the skin layer thickness to increase because the demixing of the casting solution is delayed.

The addition of organic pore former such as PEG and PVP (Al Malek *et al.*, 2012; Zaini *et al.*, 2014) to casting solutions induces higher water permeability without decreasing the membrane performance. The simple approach to understanding the function as organic pore former is to increase the pore size and indirectly enhanced the porosity of membrane skin layer. The most important property of all organic pore former is their solubility in water, which makes them ideally suitable to be used in countless different applications.

2.5.3.2 Inorganic additives

Alternatively, inorganic pore former can be applied. The concept of mixed matrix membrane (MMM) is introduced where a small filler material is dispersed throughout a larger polymeric matrix. It has brought new degrees of freedom to the development of advanced membrane materials for numerous separation processes (Koros, 2004). A new class of MMMs has been discovered and it is evaluated for potential application in ultrafiltration separations. Various inorganic particles in nanometer as well as micrometer sizes such as silica (SiO_2), zinc (ZnO), graphite (GO) and titania (TiO_2), have been blended with a variety of polymers (e.g., polysulfone (PSf), polyvinylidene fluoride (PVDF) to fabricate inorganic-organic hybrid ultrafiltration membranes (Mierzwa *et al.*, 2013; Zhang *et al.*, 2012; Liang , *et al.*, 2012).

Recently, the incorporation of ZnO nanoparticle into polyvinylidene fluoride (PVDF) has demonstrated the presence of anti-reversible fouling features (Liang *et al.*, 2012). The presence of ZnO nanoparticle could distort the morphology structure (as in Figure 2.7). This modification of inner surface directly influences the anti-reversible fouling property of the membranes.

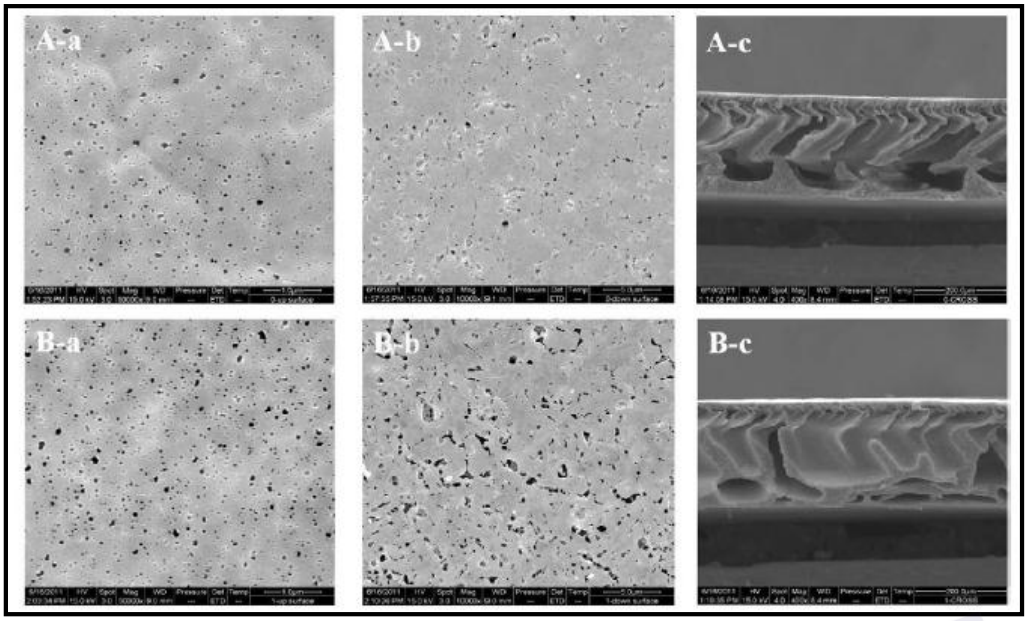

Figure 2.7 : The (a) top, (b) bottom and (c) cross-section views of PVDF membrane (A) without ZnO nanoparticle, (B) existing of ZnO nanoparticle (Liang *et al.*, 2012)

However, the addition of inorganic additives into polymer membrane is strictly controlled in order to deliver a great performance. Overloading additives resulted in compression of pore membrane due to the high viscosity of dope solution. It has been proven by Yang *et al.*, (2007) where the increase in viscosity of the casting solution supresses the macrovoid at higher additives concentration. This fact is interpreted in terms of adsorption between exposed hydroxyl group of TiO2 with high specific surface area and surface energy towards polymeric chain (Aerts *et al.*, 2000). This situation is basically correlated with viscosity condition of dope polymer solution during phase inversion process due to the development of thicker skin layer. Whenever the polymers are in high viscosity, the formation of thicker skin layer is formed easily due to slower demixing processes and aggregate formation during phase inversion processes. Thus, the amount of filler loading also plays an important role to form the most suitable and desired membrane based on the requirement application.

Study by Hamid *et al.,* (2011) which explored the performance of PSf UF incorporated with TiO2 particles membrane on antifouling and flux properties has resulted in few conclusions::

i. The PSF/TiO_2 membrane exhibited less fouling sensitivity to HA deposition than pristine membrane
ii. PSf/TiO_2 membrane which is smoother and more hydropilic surface showed lower retention time in which the lower retention time, the lower propensity for membrane to foul
iii. PSf/TiO_2 potrayed higher permeate flux in accordance to the increasing of membrane pore size
iv. HA rejection was found to have great ability to remove HA in function of filtration time

Koseoglu-Imer *et al.,* (2013) have reported the adhesion of real activated sludge on polymeric membrane incorporated silver nanoparticles (AgNP) gives a great effect to avoid fouling mechanism. The results revealed that the membranes deposited with AgNP showed lower absorptive and poor fouling value than pristine PSf membrane. It was found that foulants adhered more on membrane with high surface roughness, less hydrophilicity, and larger pore size. All of these situations suggested that the addition of inorganic additive could increase the flux and rejection as well as overcome fouling mechanism.

Instead of the amount of additives, the main point that could be focused is the type of inorganic additives also strongly influences the membrane performance. Apart from inorganic aforementioned, the incorporation of zeolite into polymer membrane as inorganic additives has received much attention. This will be discussed in the next subsection regarding the MMMs incorporated with zeolite in order to give a great performance of membrane for water filtration application.

2.6 Zeolite

Generally, zeolites are hydrated crystalline aluminosilicates which composed of tetrahedral TO4 units (T=Si or Al) which are linked together by sharing oxygen atom to form regular intracrystalline cavities and channels of aromic dimensions (Dey *et*

al., 2013). The frameworks are composed of [SiO4]4- and [AlO4]5- tetrahedra, which corner-share to form different open structures with an overall negative charge, which are balanced by the cations that can move freely in and out of its framework (Ríos Reyes, 2008). Hence, a positive extra-framework cation such as sodium (Na+) is built-in as a charge counter-balance, and gives the zeolite its ion exchange feature. Furthermore, Löwenstein's rule states that (four Si atoms can surround each Al atom, while up to four Al atoms can surround the Si atom) with oxygen bridges joining the Al and Si atoms, no two aluminium atoms bond to the same oxygen atom (Barrer, 1978; Weitkamp, 2000).

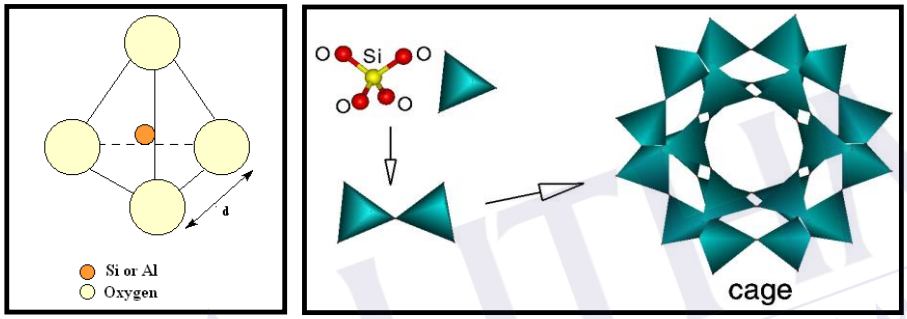

Figure 2.8 **:** Tetrahedral units for the zeolite structures (Weitkamp, 2000)

To extract the zeolite, basically it was based on empirical formula for a zeolite that would be:

$$M_{2/n}O: Al_2O_3: xSiO_2:yH_2O \qquad (2.2)$$

where M represents the charge-balance cation, n represents the charge of the cation, x is generally ≥ 2, and y is the water contains in the voids of the zeolite (McCusker & Baerlocher, 2001). It is known that no two AlO4 can be linked directly by sharing their corner in the zeolite framework.

2.6.1 Zeolite in Separation Process

Lately, zeolite membrane separation has been attracting a lot of attention in terms of lower energy consumption compared to the conventional distillation process. Since zeolite as inorganic material can show mechanical, chemical, and thermal stability, its installation into the separation process is very promising. Various types of zeolite membranes such as zeolite LTA (A) (Kondo *et al*., 2003; Wang *et al*., 2009), zeolite

FAU (X and Y) (Rasouli *et al*.,2012; Kita *et al.,* 2001; Sato *et al*., 2008, Kita *et al.,* 1997; Zhou *et al.,* 2012; Korelskiy *et al*., 2015) , mordenite (Zhou *et al*., 2012), zeolite T (Zhou *et al*., 2013) and MFI (ZSM-5 and silicalite) (Zhu *et al.*,2012 ;Yuan *et al*., 2004) have been widely studied in order to separate water/organic or organic/organic mixtures. NaA zeolite membrane was commercialized for dehydration of some organic solvents (Morigami *et al*., 2001).). However, NaA zeolite membranes are unstable in the solution containing even a trace of acid and high-concentration water (>20 wt.%) at pervaporation (PV) process by strong dealumination since its framework owns the highest alumina content among the reported zeolite frameworks (Hasegawa *et al*., 2010).

NaY zeolite (FAU framework) has a larger pore of 0.74nm, hydrophilic property, and ion exchange property, which are related to the separation performance and can be changed by adjusting the Si/Al ratio. Thus, many efforts have been mode on the dehydration, gas separation and organic separation. For dehydration, high water permeance ($2x10^{-6}$ mol m^{-2} s^{-1} Pa^{-1}) and high separation factor (a = 10,000) were achieved in dehydration of ethanol (90 wt.%)/water (10 wt.%) mixture by PV process using NaY zeolite membrane (Zhu *et al.*,2009). For gas separation, Hasegawa *et al*. (2001) has studied the effects of ion exchange of Natrium (Na), Lithium (Li), Kalium (K), Rubidium (Rb), and Caesium (Cs) cation on the separation of CO_2/N_2 -mixture using Y type zeolite membrane and showed that the highest separation factor (aCO2/N2 = 40) was obtained in the Rb exchange membrane. For separation of organic mixture, Nikolakis *et al* have carried out PV for saturated/unsaturated hydrocarbon mixture and showed high separation factor (a = 144) for benzene/n-hexane using NaX zeolite membrane. Although zeolite has been widely used in PV, the rare investigation of Y zeolite is carried out in the UF process.

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